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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: Yasushi Akiyama

Serial No.: 10/518,105

Group Art Unit: 1795

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Examiner: Ponder N. Thompson-Rummel

For: Process for preventing development defect and composition for use in the same

Commissioner for Patents

P. O. Box 1450

Alexandria, VA 22313-1450

DECLARATION UNDER 37 C. F. R. § 1.132

I, Yasushi AKIYAMA, a Japanese citizen, residing in Kakegawa-shi, Japan, declare as follows:

I received a Bachelor of Science degree from Yokohama City University in March, 1999 and a Master of Science degree in organic chemistry from Yokohama City University in March, 2001. I had been employed by Clariant (Japan) K.K. as a research & development engineer from April, 2001 to October, 2004, and then, I have been employed by AZ Electronic Materials (Japan) K.K. as a research & development engineer since October, 2004. I have been involved in research and development work relating to photoresists and ancillary chemicals since 2001.

I have been named as an inventor on at least 2 US pending Patents and 4 Japanese pending patent applications. I am an applicant in the above-mentioned patent application and an inventor of the invention claimed therein. I am familiar with the Takano reference which was used in the rejection of the claims in the above application.

The following experiments were performed by me or under my direction and control. The experiments were conducted to demonstrate that as the ratio of tetramethylammonium hydroxide to acid is increases, the film loss also increases.

EXPERIMENTAL REPORT

Test

Example 1 (taken from present application, bottom of page 18 to top of page 20)

1.0 parts by weight of polyacrylic acid (PAA) having weight average molecular weight of 3,000 as determined by polystyrene standards as a water-soluble polymer, 1.65 parts by weight of perfluoro-octylic acid ($C_7F_{15}COOH$) (PFOA) as an organic acid, 0.33 parts by weight of tetramethylammonium hydroxide (TMAH) (equivalent ratio (mole) of organic acid and base is 1:0.9) as a base were mixed up. Pure water was added thereto to make the total amount 100 parts by weight. Then, the solution was solved homogeneously at room temperature, and filtered with a 0.1 μm -filter to obtain the composition for preventing development-defects.

On the other hand, a positive-working photoresist comprising acetal type polymer manufactured by Clariant (Japan) K.K. (AZ DX3301P, 'AZ' is a registered trade mark.) was applied on an 8 inches silicon wafer by a spin coater made by Tokyo Electron Co. (Mark 8). It was pre-baked on a hot plate at 90°C for 90 seconds to form a photoresist film of 480 nm in thickness on a silicon wafer. The film thickness was measured by film thickness measuring equipment SM300 manufactured by Prometric Co.

Subsequently the above described composition for preventing development-defects was applied on the photoresist film by using the same spin coater as the above. It was then pre-baked on a hot plate at 90°C for 60 seconds to form a film for preventing development-defects on a photoresist film of 450 Å in thickness. Next, exposure to light was conducted by using KrF reduced projection exposure equipment, FPA 3000-EX5, PEB was conducted on a hot plate at 110°C for 60 seconds. Using alkali developer, AZ 300MIF Developer (2.38 weight % tetramethylammonium hydroxide aqueous solution; 'AZ' is a registered trade mark.) as a developer, it was paddle-developed on the condition of 23°C for 1 minute, to obtain a resist pattern having 1:1 line and space width. And also the film thickness after development was measured using the same equipment as one described above. The amount of film reduction in thickness was obtained by deducting the film thickness after development

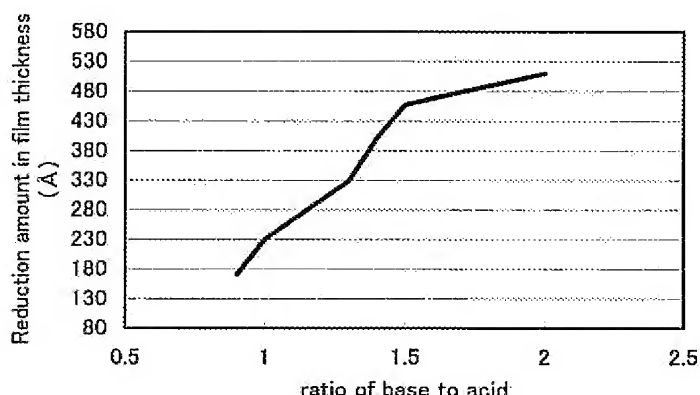
from one before development. The cross sectional form of the formed resist pattern was observed by Scanning Electronic Microscope (SEM). Observation result of the cross-sectional form of the resist pattern and the amount of film reduction in thickness are shown in the Table-1 and Graph-1 described below.

Examples 2 to 6

The same manner was taken as in Example-1 except that the equivalent (mole) ratios of base were made as described in Table-1. The results are shown in Table-1 and Graph-1 below.

Table-1. PAA(polymer), TMAH(base), PFOA(acid)

| | Acid | Base | Reduction amount in film thickness (Å) | Pattern Profile |
|-----------|------|------|--|--------------------|
| Example 1 | 1 | 0.9 | 171 | almost rectangular |
| Example 2 | 1 | 1 | 230 | almost rectangular |
| Example 3 | 1 | 1.3 | 329 | rectangular |
| Example 4 | 1 | 1.4 | 401 | rectangular |
| Example 5 | 1 | 1.5 | 458 | almost rectangular |
| Example 6 | 1 | 2 | 510 | almost rectangular |



Graph-1. PAA(polymer), TMAH(base), PFOA(acid)

Example 7

1.0 parts by weight of polyacrylic acid having weight average molecular weight of 3,000 as determined by polystyrene standards as a water-soluble polymer, 1.8 parts by

weight of perfluorooctanesulfonic acid ($C_8F_{17}SO_3H$) (PFOS) as an organic acid, 0.22 parts by weight of monoethanolamine (MEA) (equivalent ratio (mole) of organic acid and base is 1:1) as a base were mixed up. Pure water was added thereto to make the total amount 100 parts by weight. Then, the solution was solved homogeneously at room temperature, and filtered with a 0.1 μm -filter to obtain the composition for preventing development-defects.

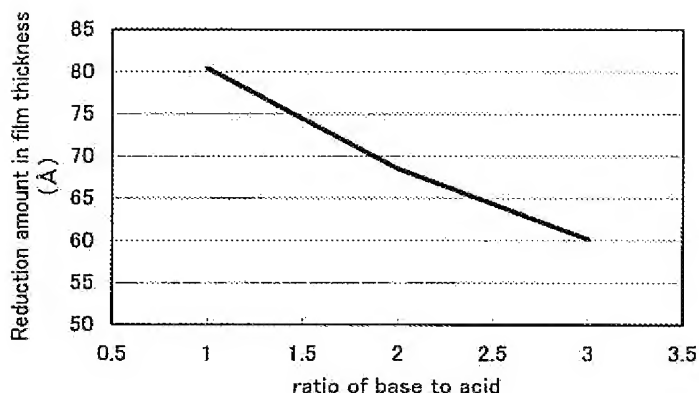
In the same manner as in above described Example 1, the silicon wafer on which a positive-working chemically amplified photoresist was applied was prepared. Then, coating above described composition for preventing development-defects on the photoresist film, exposure to light, PEB and development were conducted in the same manner as in Example 1 and a pattern form of resist cross section was observed and the amount of reduction in film thickness was measured. The result is shown in Table-2 and Graph-2 described below.

Examples 8 and 9

The same manner was taken as in Example 7 except that the equivalent (mole) ratios of base were made as described in Table-2. The results are shown in Table-2 and Graph-2 below.

Table-2. PAA(polymer), MEA(base), PFOS(acid)

| | Acid | Base | Reduction amount in film thickness (\AA) | Pattern Profile |
|---------|------|------|---|-----------------|
| Example | 1 | 1 | 80.4 | T-top |
| Example | 1 | 2 | 68.5 | T-top |
| Example | 1 | 3 | 60.2 | T-top |



Graph-2. PAA(polymer), MEA(base), PFOS(acid)

Example 10 (based on Example 1 of Takano JP 2002-006514)

1.0 parts by weight of Polyvinylpyrrolidone (PVP) having weight average molecular weight of 45000 as determined by polystyrene standards as a water-soluble polymer, 1.8 parts by weight of perfluorooctanesulfonic acid ($C_8F_{17}SO_3H$) as an organic acid, 0.22 parts by weight of monoethanolamine (MEA) (equivalent ratio (mole) of organic acid and base is 1:1) as a base were mixed up. Pure water was added thereto to make the total amount 100 parts by weight. Then, the solution was solved homogeneously at room temperature, and filtered with a $0.1 \mu m$ -filter to obtain the composition for preventing development-defects. In the same manner as in above described Example 1, the silicon wafer on which a positive-working chemically amplified photoresist was applied was prepared. Then, coating above described composition for preventing development-defects on the photoresist film, exposure to light, PEB and development were conducted in the same manner as in Example 1 and a pattern form of resist cross section was observed and the amount of reduction in film thickness was measured. The result is shown in Table-3 and Graph-4 described below.

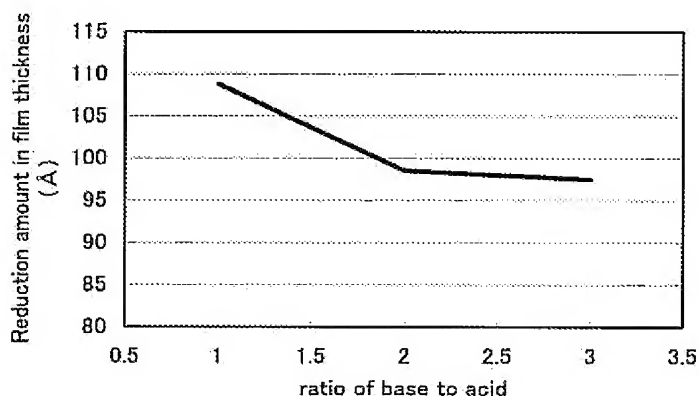
Example 11 to 12

The same manner was taken as in Example 10 except that the equivalent (mole) ratios of base were made as described in Table-3. The results are shown in Table-3 and

Graph-3 below.

Table-3. PVP(polymer), MEA(base), PFOS(acid)

| | Acid | Base | Reduction amount in film thickness (Å) | Pattern Profile |
|------------|------|------|--|-----------------|
| Example 10 | 1 | 1 | 108.8 | T-top |
| Example 11 | 1 | 2 | 98.5 | T-top |
| Example 12 | 1 | 3 | 97.5 | T-top |



Graph-3. PVP(polymer), MEA(base), PFOS(acid)

Results

As shown in the above Graphs-2 and 3, in the prior art, the equivalent (mole) ratio of base (for Example: MEA) has to be lower than that of acid to increase the film loss of photoresist film. The data in Tables-2 and 3 also show that when the equivalent (mole) ratio of base is lower than that of acid, poor pattern profile (T-Top) occurs.

In the present invention, when TMAH is used as base, the equivalent (mole) ratio of base to acid has to be higher to increase the film loss as shown in the above Graph-1. Also, the data in Table-1 show perfect or virtually perfect pattern profile (rectangular or almost rectangular).

Such results are unexpected.

I declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true, and further, that

these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both (18 U.S.C. 1001) and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Feb 26th, 2000

(date)

Yasushi Akiyama

Yasushi AKIYAMA